

# PATENT SPECIFICATION

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## (54) MODIFYING WATER-PERMEABLE POLYMERS

(71) We, KODAK LIMITED, a Company registered under the Laws of Great Britain, of Kodak House, Kingsway, London W.C.2., do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of modifying organic water-permeable polymers.

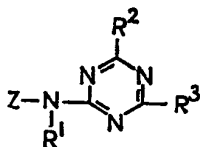
According to the present invention there is provided a method of modifying a synthetic or semi-synthetic (as hereinafter defined) organic water-permeable polymer which comprises causing the polymer to react by means of heat and/or exposure to other forms of radiant energy with a polymer modifying compound which is free of polymerizable vinyl group and contains a single azido group attached to an aromatic carbocyclic or heterocyclic ring or at least one  $-\text{CON}_3$ ,  $-\text{SO}_2\text{N}_3$ ,  $>\text{N}-\text{SO}_2\text{N}_3$  or  $-\text{SON}_3$  group or at least one  $-\text{CH}(\text{Hal})_2$  or  $-\text{C}(\text{Hal})_3$  group attached to an aromatic carbocyclic or heterocyclic ring wherein Hal is a halogen atom but excluding  $-\text{CHF}_2$  and  $-\text{CF}_3$  groups.

The groups listed above are referred to herein as "reactive groups".

Although the mechanism of reaction is not fully understood it is believed that the reaction proceeds by the formation of a short lived intermediate which is, respectively a carbene, nitrene or, in the case of  $-\text{CH}(\text{Hal})_2$  and  $-\text{C}(\text{Hal})_3$  groups, a different free radical, which inserts into a C—H bond of the polymer.

The reactive group may be attached directly to an aromatic ring, e.g. a carbocyclic or heterocyclic aromatic ring. In a preferred embodiment of the present invention the modifying compound contains an  $-\text{N}_3$  group attached to a carbon atom of a benzene, naphthalene, pyrimidine or s-triazine ring. In other embodiments the modifying compound contains a  $-\text{CHBr}_2$  or  $-\text{CBr}_3$  group attached to the 2-position of a quinoline ring or an  $-\text{SO}_2\text{N}_3$  group attached to a benzene ring.

A preferred class of compounds for use in the present invention have the general formula:—



wherein

Z is the residue of a dye, fluorescent brightener or U.V. absorber,

R<sup>1</sup> is a hydrogen atom or an alkyl or aryl group,

R<sup>2</sup> is an azide or azidophenoxy group,

R<sup>3</sup> is a dialkylamino or Z—NR<sup>1</sup>— group or a chlorine or bromine atom.

By the term "semi-synthetic" as applied to polymers we mean a polymer of natural origin which has been modified by synthetic means, for example, carboxymethyl cellulose or an acylated gelatin. The water-permeable polymer may also

be water-soluble. Examples of water-permeable synthetic or semi-synthetic polymers which may be modified by the present method include: polyvinyl alcohol, a water-permeable acrylic polymer or copolymer, e.g. polymers containing units of acrylic acid, ethyl acrylate or acrylamide, carboxymethyl cellulose or an acylated gelatin, e.g. phthalated gelatin.

The polymer modifying compound may modify any chemical or physical property of the polymer including surface properties. The modifying compound may be a dye, pigment, fluorescent brightening agent, UV absorber, IR absorber stabilizer, antioxidant, or antistatic compound. It may also be a silver halide developing agent precursor or a photographic colour coupler precursor. It may contain one or more water-solubilizing groups.

The present invention also provides a photographic material which contains a layer comprising a modified polymer according to the invention. The layer may also comprise gelatin or other hydrophilic colloid. Preferred materials contain a light-sensitive silver halide emulsion layer. In this case the present invention provides a method of incorporating photographic addenda or their precursors in hydrophilic colloid layers and rendering them non-wandering by attaching them chemically to the colloid. These layers may also contain other hydrophilic colloids, e.g., gelatin. Such photographic addenda may be, for example, developing agents, development accelerators, antifoggants, antistain agents, hardeners, toners, antibronzing agents, covering power improving agents, restrainers, colour couplers, competing couplers, developer inhibiting releasing couplers and dyes which filter, absorb, fluoresce or sensitise.

The polymer and the modifying compound may be mixed together preferably in solution or, alternatively, the polymer may be immersed in a solution or suspension of the modifying compound prior to causing them to react. Alternatively the modifying compound may be mixed with an appropriate monomer or mixture of monomers containing a polymerisable vinyl group and the reaction effected during polymerisation. Additional reaction may be effected, if required, by heating the polymer so formed.

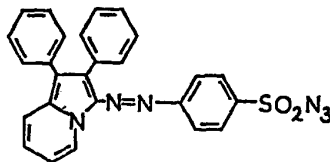
The reaction may be induced by heating the polymer and modifying compound preferably in the solid state to a temperature below that at which the polymer will degrade and/or by exposing them to UV radiation, microwave radiation, visible light, X-rays, gamma rays or electron bombardment.

Dyes, fluorescent brightening agents and other modifying compounds containing the reactive groups are described in our copending Application Nos. 15514/70 (Serial No. 1344992), 15169/70 (Serial No. 1344991) and 21281/70 (Serial No. 1344993). They may be prepared by methods known, in general, to the skilled organic chemist.

The invention is illustrated by the following Examples.

#### Example 1

A red dye of the formula:



( $4.8 \times 10^{-2}$  grams), and 8.6 grams of a copolymer of ethyl acrylate/acrylic acid (4:1 molar) were dissolved in tetrahydrofuran (100 mls.). The solvent was allowed to evaporate off. When heated for 30 minutes in the solid state at  $175^{\circ}\text{C}$  31% of the dye grafted onto the copolymer. Unreacted dye was extracted with benzene. When the same quantities were irradiated using a medium pressure UV lamp for 3 minutes 22% of the dye grafted onto the hydrophilic polymer.

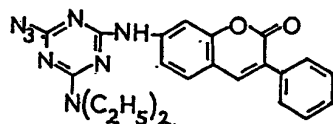
The product is capable of being dispersed in gelatin which can be employed to form anti-halation or light-absorbing layers as part of a photographic material.

#### Example 2

A copolymer of ethyl acrylate and acrylic acid (4:1 molar) (9.5 gram) and

the brightener A (0.2 gram) were dissolved in tetrahydrofuran (100 mls.). The solvent was evaporated off.

A



When heated for 30 minutes at 200°C under vacuum, 61% of the brightener grafted onto the copolymer. Unreacted brightener was extracted with benzene.

When the same quantities were irradiated using a medium pressure UV lamp for 5 minutes, 23% of the brightener grafted onto the hydrophilic polymer.

The product is capable of being dispersed in gelatin which can be employed to form a layer which is part of an optically brightened photographic material.

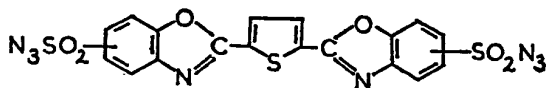
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#### Example 3

A copolymer of ethyl acrylate and acrylic acid (4:1 molar) (9.3 grams) and the brightener B (0.01 gram) were dissolved in tetrahydrofuran (100 mls). The solvent was evaporated off. When heated for 10 minutes at 170°C under nitrogen, 35% of the brightener grafted onto the polymer. Unreacted brightener and yellow bi-product were extracted with benzene.

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B



The product is capable of being dispersed in gelatin which dispersion can be employed to form a layer, part of an optically brightened photographic material.

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#### Example 4

(a) Acrylic acid monomer (20 mls) the brightener A as is Example 2 (0.02 gram) and an initiator azo - bis - iso - butyronitrile (0.1 gram) were mixed and degassed under vacuum. The mix was allowed to polymerise at 50°C until solid (about 20 minutes). The temperature was raised to 184°C during 2 hours and maintained there for 15 to 20 minutes. The cooled product was dissolved in dioxane (400 mls) and precipitated with *n*-hexane (1500 mls). 37% of the brightener had grafted onto the polyacrylic acid.

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(b) By the same procedure, but heating finally at 205°C for 1 hour, 58% of the brightener was caused to graft onto the polyacrylic acid.

(c) Using the brightener A (0.07 gram) in the same mix, and heating at 178°C for 30 minutes caused 49% of the brightener to graft onto the polyacrylic acid.

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The products (1 gram) dissolved in a 5% by weight aqueous gelatin solution (50 mls) by neutralizing with sodium hydroxide to pH 7 were coated onto a support and allowed to dry. The resulting layers were fluorescent, and could form part of an optically brightened photographic material.

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#### Example 5

Vinylpyrrolidone monomer (20 mls), the brightener A as in Example 2 (0.1 gram) and an initiator azo - bis - isobutyronitrile (0.1 gram) were mixed and degassed under vacuum. The pale green mix was allowed to polymerise at 70°C until solid (overnight). The temperature was raised to 180° during 2 hours and held there for 30 minutes.

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The cooled product was dissolved in acetone (400 mls.) and precipitated with *n*-hexane (1500 mls). 50% of the brightener had grafted onto the polyvinylpyrrolidone. The product was obtained as a bright green solid which became blue/white on acidification.

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The product (1 gram) dissolved in a 50% aqueous gelatin solution (50 mls) was coated onto a support and allowed to dry. The resulting layer was fluorescent and could form part of an optically brightened photographic material.

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## Example 6

Acrylamide monomer (20 grams), the brightener A as in Example 2 (0.2 gram) and the same initiator (0.1 gram) used in Example 5 with isopropyl alcohol (4.4 mls), dioxane (50 mls) and water (10 mls) were mixed and degassed under vacuum. The solution stood overnight at room temperature. It polymerised to a curdy suspension. The solvent was removed under vacuum, and the temperature was raised to 180° during 2 hours and kept there for about 30 minutes.

The cooled product was dissolved in water (200 mls) and precipitated with acetone (1500 mls). This was repeated and the product (10 grams) freeze-dried. 6% of the brightener had grafted onto the polyacrylamide.

The product is capable of being dissolved in an aqueous gelatin solution which can be employed to form a layer which is part of an optically brightened photographic material.

## WHAT WE CLAIM IS:—

1. A method of modifying a synthetic or semi-synthetic (as hereinbefore defined) organic water-permeable polymer which comprises causing the polymer to react by means of heat and/or exposure to other forms of radiant energy with a polymer modifying compound which is free of polymerizable vinyl groups and contains a single azido group attached to an aromatic carbocyclic or heterocyclic ring or at least one —CON<sub>3</sub>, —SO<sub>2</sub>N<sub>3</sub>, —N—SO<sub>2</sub>N<sub>3</sub> or —SON<sub>3</sub> group or at least one —CH(Hal)<sub>2</sub> or —C(Hal)<sub>3</sub> group attached to an aromatic carbocyclic or heterocyclic ring wherein Hal is a halogen atom but excluding —CHF<sub>2</sub> and —CF<sub>3</sub> groups.

2. A method as claimed in Claim 1 in which the polymer modifying compound contains a said azido —CON<sub>3</sub>, —SO<sub>2</sub>N<sub>3</sub>, —CH(Hal)<sub>2</sub> or —C(Hal)<sub>3</sub> group wherein Hal is as defined in Claim 1.

3. A modification of the method according to Claim 1 or 2 in which the modifying compound is mixed with an appropriate monomer or mixture of monomers containing a polymerisable vinyl group and the reaction is effected during polymerisation of the monomer(s) and in which optional additional reaction is effected by heating the polymer so formed.

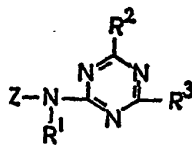
4. A method as claimed in any of Claims 1—3 in which the reactive group (as hereinbefore defined) is attached to an aromatic ring of the polymer modifying compound.

5. A method as claimed in any of Claims 1—4 in which the modifying compound contains an —N<sub>3</sub> group attached to a carbon atom of a benzene, naphthalene, pyrimidine or s-triazine ring.

6. A method as claimed in any of Claims 1—4 in which the modifying compound contains a —CHBr<sub>2</sub> or —CBr<sub>3</sub> group attached to the 2-position of a quinoline ring.

7. A method as claimed in any of Claims 1—4 in which the modifying compound contains an —SO<sub>2</sub>N<sub>3</sub> group attached to a benzene ring.

8. A method as claimed in any of Claims 1—5 in which the modifying compound has the general formula:



wherein

Z is the residue of a dye, fluorescent brightener or U.V. absorber,

R<sup>1</sup> is a hydrogen atom or an alkyl or aryl group,

R<sup>2</sup> is an azide or azidophenoxy group,

R<sup>3</sup> is a dialkylamino or Z—NR<sup>1</sup>— group or a chlorine or bromine atom.

9. A method as claimed in any of Claims 1—8 in which the polymer modifying compound is a dye, fluorescent brightening agent, silver halide developing agent precursor or photographic colour coupler precursor.

10. A method as claimed in any of Claims 1—9 in which the reaction is effected in the solid state.

11. A method according to Claim 1 or 3 substantially as described herein and with reference to the Examples.

12. An organic water-permeable polymer modified by the method of any one of Claims 1—11.

13. A photographic material which includes a layer comprising a polymer as claimed in Claim 12.

5 14. A photographic material as claimed in Claim 13 in which the layer further comprises gelatin or other hydrophilic colloid. 5

15. A photographic material as claimed in Claim 13 or 14 which also contains a light-sensitive silver halide emulsion layer.

16. A photographic material substantially as described herein.

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